

46th Heyrovský Discussion

**MOLECULAR ELECTROCHEMISTRY
IN ORGANOMETALLIC SCIENCE**

Book of Abstracts



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Synthesis and Electrochemical Studies of Rhenium(I) and Molybdenum(0) Complexes as Electrocatalysts for Reduction of Carbon Dioxide

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The photochemical and electrochemical conversion of CO₂ to higher-energy products has been a focus of research as a path to renewable fuels. This thermodynamically unfavorable process can be improved by employing transition-metal coordination compounds which, in the form of molecular or supramolecular organometallic catalysts, are capable of mediating CO₂ reduction. Among them, we focused on Rhenium and Molybdenum. However, whereas a wide number of Rhenium(I) carbonyl-diimine complexes showed to be photo/redox active, and has already been successfully tested for the electrocatalytic CO₂ reduction, to our knowledge, there are no reports about the use of tetracarbonyl polypyridyl molybdenum(0) complexes as electrocatalysts for the reduction of CO₂. In this perspective, some [Mo(CO)₄(L)] (L= 2,2'-bipyridine (bpy); 1,10-phenantroline (phen) and similar derivatives) were synthesized and tested for electrochemical reduction of carbon dioxide. Moreover, a series of novel Re(I)-carbonyl diimine complexes has been synthesized and tested for the same purpose. The latter class of compounds is characterized by new polypyridyl ligands, derived from PNI-phen (N-(1,10-phenantroline)-4-(1-piperidinyl)naphthalene-1,8-dicarboximide), which revealed to be able to provide a 3000-fold excited state lifetime enhancement in a Re(I) charge-transfer complex [1]. The electrochemical behavior of both the classes of compounds was compared with the activity of Re(CO)₃Cl(bipy) [2].

Quite surprisingly, CV measurements (in MeCN and acetone), performed under both inert and CO₂ atmosphere at room temperature, revealed that [Mo(CO)₄(2,2'-bipyridyl)] shows redox activity as electrocatalyst for CO₂ reduction, although the overpotential at which the process occurs is rather negative (about -1.9 V vs SCE). The catalytic activity was also confirmed by controlled-potential electrolysis at -1.80 V, coupled with gas chromatography (GC).

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